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Analysis of electronic and optical losses in $Cu(In,Ga)Se_2$/dye sensitized cell tandem solar cells

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Abstract

To optimize dual junction solar cells using a dye-sensitized cell (DSC) as top cell and a $Cu(In,Ga)Se_2$ (CIGS) cell as bottom cell, both optical and electronic loss mechanisms were investigated. The light absorption and optical losses in various layers were investigated through transmission measurements, and the amount of light available for photogeneration of charge carriers was determined. From the measured light balance, a maximum possible current for the cells was estimated. I-V curves of stacked solar cells were analyzed to investigate possible electronic loss mechanisms. From the results gained in these measurements, conclusions about the limiting factors and potential optimizations in DSC/CIGS tandem solar cells could be drawn. Calculations showed that current densities up to 20 $mAcm^{-2}$ can be generated in a CIGS bottom cell with the light transmitted from the DSC. This would correspond to an efficiency exceeding 20%, given that highly transmitting DSCs yielding such high currents can be provided.

Keywords: solar cells; CIGS; dye sensitized cells; tandem cells; loss mechanism

1. Introduction

$Cu(In,Ga)Se_2$ (CIGS)-based thin film solar cells have up to now yielded efficiencies of up to 19.9% [1]. However, single junction solar cells do not use the solar spectrum in an optimal way as all the photon energy higher than the bandgap is lost to thermalization of the charge carriers with the crystal lattice of the absorber [2]. This limitation can be overcome by the serially connected stack of solar cells with different absorption properties. For dual junction solar cells, as studied in this paper, the optimum bandgaps are 1.0 to 1.3 eV and 1.6 to 1.75 eV for bottom and top cells, respectively [3]. Such multijunction solar cells are already widely used in high-end III-V

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devices as well as in amorphous/microcrystalline Si based solar cells. Up to now, the highest reported efficiencies for solar cells of 40.1% under concentrated light and 33.8% under one-sun illumination were measured using GaInP/GaAs/GaInAs and GaInP/GaInAs/GaInAs triple junction cells, respectively [4].

However, to achieve the maximum possible efficiency in serially connected stacked multijunction solar cell, it is essential to match the current generated in top and bottom cells as the overall current in a series connection is determined by the lowest contributing current in the circuit. Thus, due to the possibility of bandgap engineering in a CIGS solar cell by changing the [Ga]/[In+Ga] ratio of the absorber, the current generated here can be easily adjusted. With the high spectral response in the red and near infrared region of the solar spectrum, these absorbers make a good choice for a bottom cell in a dual junction device.

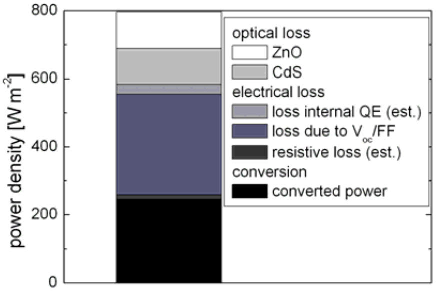

Figure 1: Origin of power losses in a CIGS solar cell.

Dye-sensitized solar cells (DSCs) can be produced with a wide variety of sensitizers of different absorption characteristics and the thickness of the sensitized TiO_2 layer can be varied which influences both transparency and generated photocurrent. Cells of this type typically show their best response in the visible range of the spectrum and thus are optimum top cells [5].

Manufacturing the DSCs on high mobility TCOs such as In2O3:Ti (ITiO) or In2O3:Mo (IMO) can help to increase the current density generated in the bottom cell. Due to the high mobility of the charge carriers in the TCO, the carrier concentration can be significantly reduced while maintaining good conductivity, thus substantially reducing the optical losses by free charge carriers in the infra-red region [6].

In earlier works, we have shown that current matching is essentially possible between DSCs and CIGS-cells [7] and demonstrated the concept of a monolithically integrated DSC/CIGS tandem solar cell [8]. To maximize the efficiency of the whole stack, some optical and electronic loss analysis is presented in this paper.

2. Experimental

CIGS absorbers investigated in the present paper were produced using coevaporation of elements in a multi-stage evaporation process, the thickness of the absorbers was about 1.8 µm. As a substrate, soda-lime glass (SLG) coated with a bilayer of dc-sputtered molybdenum was used. Na was incorporated into the layer by diffusion from the glass substrate through the Mo. Substrate temperature was varied between 400 °C and 580 °C in the different stages of the growth process.

As buffer layer, chemical bath deposited CdS with a thickness of 50 nm was used, followed by a transparent front contact consisting of intrinsic ZnO (50 nm) and 300 nm of ZnO:Al deposited by rf-sputtering. To enhance current collection, a Ni/Al grid was deposited on top by e-beam evaporation.

Finally, on each 5x5 cm^2 glass substrate, 32 cells of 0.6 cm^2 each were isolated by mechanical scribing.

For transmission measurements, the respective layers were deposited onto glass and measured with an uncoated SLG sheet as reference to subtract the absorption of the substrate.

3. Current Estimation Calculations

To estimate the maximum possible current in the CIGS solar cell, simple calculations were performed. As the solar spectrum is given as the irradiation power density per wavelength p, the total irradiation power density P available for energy conversion in a given wavelength interval $[\lambda_1,\lambda_2]$ can be calculated by integration as in

$$P_{irradiation} = \int_{\lambda_1}^{\lambda_2} p(\lambda)\, \mathrm{d}\lambda \tag{1}$$

where λ denotes the wavelength. The integration boundaries λ_1 and λ_2 are on the low wavelength side given by the onset of the solar spectrum, and on the long wavelength side by the optical bandgap of the CIGS absorber. The total power was then corrected by the V_{oc} losses (V_{oc} = 700 mV) and a fill factor of 70% was assumed which resulted in a further lowering of the available total power as in

$$P_{conversion} = P_{irradiation} \cdot \frac{q \cdot V_{oc}}{E_g} \cdot FF. \tag{2}$$

Finally, resistive and internal QE losses were empirically estimated with 5% each. The maximum possible current density j can then be easily calculated by

$$j = \frac{P_{conversion}}{V_{oc}}. \tag{3}$$

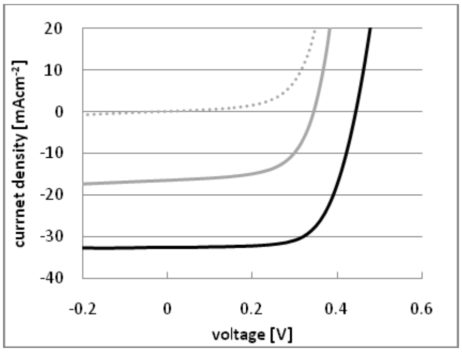

Figure 3: IV curve of a CIS bottom cell in a tandem device, under AM1.5 illumination filtered through a DSC (solid grey line) and dark curve (dotted grey line). Unfiltered IV curve is shown in the black curve.

Here, V denotes the voltage over the cell.

For realistic values, the integration boundaries used for eq. (1) were assumed with λ_1 = 300 nm and λ_2 = 1100 nm. Below 300 nm there isn't any carrier generation in the CIGS due to the absorption in the ZnO and the CdS, the 1100 nm absorption edge is corresponding to an optical bandgap of 1.13 eV, corresponding to a [Ga]/[In+Ga] ratio x = 0.20 using

$$E_g^{CIGS} = E_g^{CIS} \cdot (1-x) + E_g^{CGS} \cdot x - x \cdot (1-x) \cdot 0.2\ \text{eV}$$

as reported elsewhere [9]. E_g^A denotes the bandgap of the material A (CIS: 1.04 eV, CGS: 1.68 eV). Bandgap values were taken from Rau [3] due to low temperature bandgap values published by Yakushev et al. [9].

Any influences of multiple reflections at layer interfaces or interference effects have been disregarded for these calculations.

4. Results and Discussion

When looking at the total available power for energy conversion in a CIGS solar cell (Fig. 1), it becomes obvious immediately that most of the power loss results from the low operating voltage compared to the intrinsic voltage, i.e., the bandgap. However, also the optical losses are non-negligible. Especially when used in a tandem cell, highly transmitting contacts of the DSC are beneficial as the light made available for the bottom cell should be maximized. Using a 1.13 eV CIGS solar cell, the maximum total current as estimated with formulae (1) – (3) and using the C101-DSC transmittance curves for calculating the irradiating power density is 20.7 mAcm^{-2} with a DSC front cell using the C101 high performance dye [10] and a ITiO high mobility TCO front contact, while using a conventional SnO_2:F (FTO) or In_2O_3:Sn (ITO) front contact restricts the current to 18.7 mAcm^{-2}. This difference can be clearly attributed to the improved transmittance in the near infrared region of the spectrum between 700 and 1100 nm as illustrated in Fig. 2. Due to the higher mobility of the ITiO compared to FTO or ITO, the charge carrier density can be reduced while maintaining the same conductivity, thus reducing the free carrier absorption in the NIR region of the solar spectrum [11].

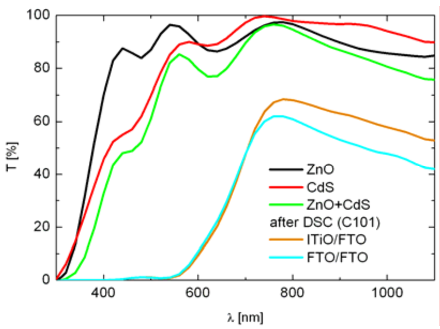

Figure 2: Transmission data of absorbing layers in front of the CIGS absorber. Top three lines correspond to the absorbing layers in the CIGS cell itself, while the two bottom lines show the absorption characteristics of a DSC on high mobility and normal TCO, respectively.

These results show that current matching between CIGS bottom cells and DSC top cells should be possible even for high-current dyes like C101, up to 19 to 20 mAcm^{-2}. With loss-free voltage adding ($V_{oc,tandem}$ = 1.4 V) and an assumed fill factor of 74% this would correspond to an efficiency of 19.7 to 20.7%, significantly exceeding the CIGS baseline efficiency in our laboratory of 16 to 17%, given such a high current can be provided by a DSC without sacrificing transmittance in the NIR region. However, when assembling a mechanically stacked solar cell, as these transmission calculations assume, there is always the drawback of having a small gap of air in between the two cells leading to reflection losses. These can be diminished by using index matching oil, but not completely overcome. Monolithically integrated tandem cells as reported by Wenger et al. [8] avoid that loss and result in a maximum possible current density increment of about 10%.

In addition to the optical absorption losses in a tandem device, one should also take care of the electronic losses in the device. First, like in every solar cell, large losses in the available power for energy conversion results from recombination of charge carriers before collection in the p-n junction, leading to a reduced open circuit voltage compared to the bandgap of the absorber. Additionally, due to leakage currents, the parallel resistance of the CIGS absorber is reduced and therefore the fill factor, and to a smaller extent the V_{oc}, deteriorates, leading to lower conversion efficiencies. In mechanically stacked cells, this can mainly be attributed to the contacting procedure: a small aluminum sheet is stuck to the Ni/Al grid of the bottom cell using silver paste, and then connected to a wire to the front cell rear contact using soldering. As silver paste is generally applied as a solution, some paste and solvent can leak to the scribes which isolate the cells. The leakage current can be seen in Fig. 3. The parallel resistance over the CIGS layer decreased an order of magnitude from 1028 Ωcm before contacting the cells to only 132 Ωcm after contacting.

In monolithically connected tandem cells, the situation is a bit more complicated. The dye sensitized solar cells use a I_3^-/I^- electrolyte for charge transportation. Both the ZnO front electrode and the CIGS absorber are corroded by that liquid, resulting in constant efficiency loss in the tandem cell and finally in a shunting of the bottom cell, such that the tandem IV curve corresponds to the IV curve of the top cell [8].

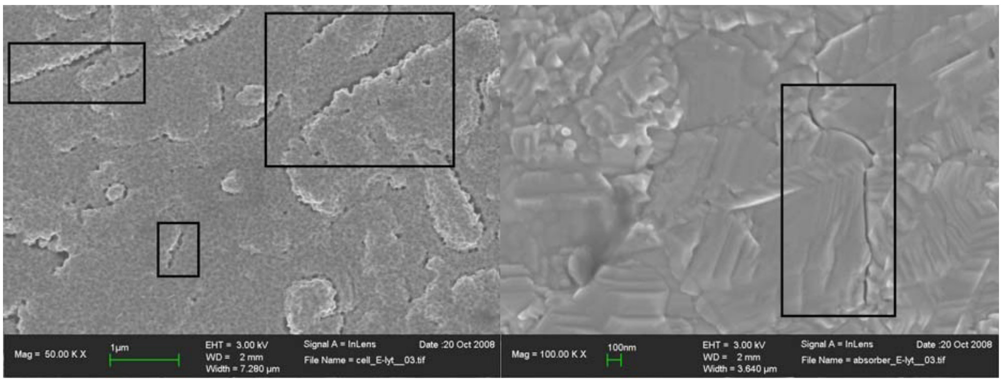

Figure 4: SEM images of a CIGS solar cell (ZnO surface, left) and a bare CIGS absorber (right) after 40 min of exposure to the I_3^-/I^- DSC electrolyte. Cracks (none visible before exposure) highlighted.

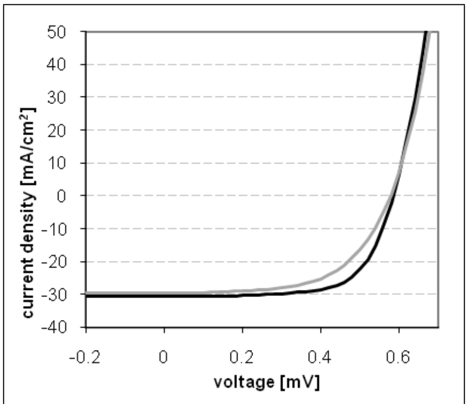

Figure 5: IV curves of a CIGS solar cell before (black) and after exposure to the DSC electrolyte.

This corrosion theory is supported by an IV measurement of a CIGS solar cell before and after exposure to the electrolyte. A drop of electrolyte was applied to the ZnO surface in air, and no sealing was applied in contrast to a DSC/CIGS tandem, resulting in a higher evaporation rate of the electrolyte and therefore reducing the effect of corrosion. Nevertheless, after 40 min of exposure, a significant loss in cell performance could be observed. IV parameters are shown in Table 1. Corresponding IV curves are shown in figure 5.

Table 1: IV parameters of a CIGS solar cell before and after 40 min exposure to I_3^-/I^- DSC electrolyte.

	J_{sc} [$mAcm^{-2}$]	V_{oc} [mV]	FF	η
before exposure	30.6	584	67.5%	12.1%
after exposure	29.6	578	59.1%	10.1%

Further evidence for the corrosion of CIGS and ZnO by the electrolyte is given by SEM images of both a finished cell and a bare absorber after being exposed to the electrolyte (Figure 4).

5. Conclusion

Calculations to estimate the maximum possible current density in CIGS solar cells used as a bottom cell in DSC/CIGS tandem solar cells were performed. Results show that matched currents of up to 20 $mAcm^{-2}$ and efficiencies exceeding 20% are theoretically possible. Absorption losses can be lessened by using high mobility TCOs such as ITiO in the DSC, and by constructing monolithically assembled tandem solar cells.

Electronic losses, other than the losses due to recombination in the absorber, are mostly attributed to technicalities in assembly. The problem of leaking currents due to contacting (stacked devices) or corrosion (monolithic devices) needs to be addressed.

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